Dynamic mechanical properties of cementitious composites with carbon nanotubes

JialiangWang[1], Sufen Dong[2], Ashraf Ashour[3], XinyueWang[1], Baoguo Han[1,*]

[1]*School of Civil Engineering, Dalian University of Technology, Dalian, 116024 China*
[2] *School of Material Science and Engineering, Dalian University of Technology, Dalian, 116024 China*
[3]*Faculty of Engineering & Informatics, University of Bradford, Bradford, BD7 1DP, UK*
* Corresponding author: hithanbaoguo@163.com, hanbaoguo@dlut.edu.cn

Abstract:

This paper studied the effect of different types of multi-walled carbon nanotubes (MWCNTs) on the dynamic mechanical properties of cementitious composites. Impact compression test was conducted on various specimens to obtain the dynamic stress-strain curves and dynamic compressive strength as well as deformation of cementitious composites. The dynamic impact toughness and impact dissipation energy were, then, estimated. Furthermore, the microscopic morphology of cementitious composites was identified by using the scanning electron microscope to show the reinforcing mechanisms of MWCNTs on cementitious composites. Experimental results show that all types of MWCNTs can increase the dynamic compressive strength and ultimate strain of the composite, but the dynamic peak strain of the composite presents deviations with the MWCNT incorporation. The composite with thick-short MWCNTs has a 100.8% increase in the impact toughness, and the composite with thin-long MWCNTs presents an increased dissipation energy up to 93.8%. MWCNTs with special structure or coating treatment have higher reinforcing effect to strength of the composite against untreated MWCNTs. The modifying mechanisms of MWCNTs on cementitious composite are mainly attributed to their nucleation and bridging effects, which prevent the micro-crack generation and delay the macro-crack propagation through increasing the energy consumption.

Keywords: C. Mechanical Properties; C. Strain Effect; D. Reinforcement; E. Composite; E. Fiber Reinforcement

1. Introduction

Cementitious composites are the most widely used building materials in the world. However, as multi-phase, multi-scale materials, cementitious composites have inevitably initial defects, greatly decreasing their mechanical properties [1]. Furthermore, cementitious composites tend to collapse once the bearing capacity is exceeded due to their brittleness and poor energy consumption, seriously affecting the safety of cementitious composite structures [2]. On the other hand, with increasing the complexity and extreme of the service environment as well as the multi-factor coupling actions, cementitious composites are facing more severe challenges [3-5]. In some infrastructures, cementitious composites are not only subjected to static loads, but also susceptible to dynamic impact loads [6-8]. Under the condition of high strain rate, the compression time of cementitious composites becomes shorter, and the effective force area of the composites decreases, resulting in the aggravation of brittleness failure of the materials [9].

In order to overcome flaws of cementitious composites under impact loads, researchers [10-14] tried to increase the compactness and ductility of the composites by adding mineral admixtures and high-strength steel fibers into cementitious matrix, thereby inhibiting the growth of cracks and improving the energy absorption capacity of the composite. However, these methods do not fundamentally inhibit the initial defects of cementitious composites, because they generate some voids or holes in the composite internal structure, inducing additional defects. In fact, big changes in the micro-macroscale behaviors of cementitious composites are predicated from the nanoscale impact. Even with small changes in the nanoscale, need-driven innovative design and production of materials and infrastructures could lead to large accumulated benefits. Therefore, it is of great significance to reduce the formation of nanoscale cracks, prevent them from growing into micron cracks, and, thus, avoid the macroscopic crack propagation.

Multi-walled carbon nanotube (MWCNT) possessing one-dimensional tubular structure is formed by crimping multiple layers of graphene sheets [15], achieving excellent mechanical properties [16, 17], high electrical conductivity [18, 19] and high thermal properties [20]. Many of the characteristics of MWCNT make it an ideal material to replace traditional fiber, aiming to develop high-energy absorbing materials with broad application prospects. Previous researchers [21-28] have reported that under static loading, the incorporation of MWCNTs significantly enhances the elastic modulus, compressive strength, flexural strength and fracture energy of cementitious composite. For example, Li et al. [21] observed that the incorporation of 0.5% of MWCNTs can increase the compressive, flexural strength and the failure strain of cementitious composites by 19%, 25% and 27%, respectively. Ibarra et al. [24] found that Young's modulus of cementitious composites is enhanced by 227% with the addition of 0.1% of MWCNTs. In addition, a 600% increase in Vickers hardness at the early hydration [29], a 14% increase in fracture energy [30], and a 270% increase in fracture toughness [31] of cementitious composites were also achieved due to the presence of MWCNTs.

However, whether MWCNTs can ensure the reinforcing effect on cementitious composites under impact loading and how the dynamic damage of composites evolves are rarely reported. Furthermore, as an important influence factor for the performances of cementitious composites, the bonding ability between MWCNTs and the composite is closely related to the dispersion quality, content level, internal structure and properties of MWCNTs [32, 33]. In fact, different physical morphology and surface modification of MWCNTs can have different effects on performances of cementitious composites. By carrying out special structural treatment and surface modification of MWCNTs, the contact area and surface activation point of MWCNTs can be further improved, which is conducive to play the nano-enhancement effect of MWCNTs, thereby enhancing the energy absorption capacity of concrete materials and then delaying the development of cracks. Therefore, it is necessary to comprehensively and systematically study the effects of different types of MWCNTs on dynamic mechanical properties of cementitious composites, analyze the reinforcing mechanisms of MWCNTs, and understand the dynamic mechanical behavior of the composite under impact compression load.

This paper studied the effects of sizes, special structures and coating treatments of MWCNTs on the dynamic mechanical properties of cementitious composites. The dynamic compressive strength and dynamic strain were obtained whereas the dynamic compression toughness was characterized. Finally, the reinforcing mechanisms of MWCNTs on cementitious composites were analyzed and the dynamic damage evolution of cementitious composites under impact loads was explained.

2. Materials and experiments

2.1 Materials and preparation

Table 1 shows the physical properties of different MWCNT types used in the current investigation. Eight different types of MWCNTs having various sizes, structures, coating treatments and specific surface areas but the same density were studied. The raw materials and mix proportion of cementitious composites with and without MWCNTs are listed in Table 2. In addition to the control mix (C0) without MWCNT, 0.25% and 0.5% of MWCNTs by weight of cement were considered for each type of MWCNT. It is of note that the material selection, mix design and specimen preparation are all based on the existing references [27, 28], which have ensured the effective dispersion of MWCNTs and the good workability of fresh concrete.

Table 1 Physical properties of MWCNTs

Types	Out diameter /nm	Inner diameter /nm	Length /μm	Specific surface area m^2/g
TL	20-30	5-10	10-30	> 110
TS	20-30		0.5-2	> 120
tL	< 8	2-5	10-30	> 350
tS	< 8	2-5	0.5-2	> 350
LIM	30-60	20-50	1-10	> 200
HIM	100-200	-	1-10	> 30
NiM	20-30	5-10	10-30	70
GM	20-30	5-10	10-30	> 90

Note: TL, TS, tL, tS, LIM, HIM, NiM and GM denote thick-long, thick-short, thin-long, thin-short, large inner thin-wall, helical, nickel-coated and graphitized MWCNTs, respectively.

Fig. 1 demonstrates the schematic diagram of specimen preparation. A standard disc mold of dimensions Φ30.0 mm×15.0 mm was used to cast specimens for impact compression test. In order to ensure the surface flatness (within 0.05 mm) of specimen, all the specimens were surface-polished with sandpaper after demolding. Before the test, the specimens were initially cured in water (25℃) for 90 days and then placed in air (room temperature) for 7 days.

Table 2 Mix proportion of composites without and with MWCNTs

Code	C	FA	SF	S	W	SP	MWCNTs
C0	0.8	0.2	0.25	1.1	0.3	1.50%	0
TL1 / TL2 TS1 / TS2 tL1 / tL2 tS1 / tS2 LIM1 / LIM2 HIM1 / HIM2 NiM1 / NiM2 GM1 / GM2	0.798 / 0.796	0.2	0.25	1.1	0.3	1.50%	0.25% / 0.50%

Note: C, S, W, SP, FA and SF denote cement, sand, water, superplasticizer, fly ash and silica fume, respectively.

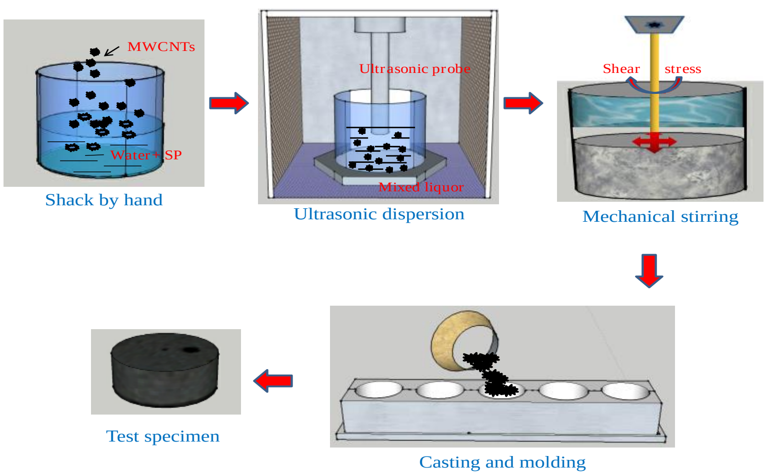


Fig. 1 Schematic diagram of specimen preparation

2.2 Experimental tests

2.2.1 Impact compression test

In this paper, the impact compression test was performed with split Hopkinson pressure bar (SHPB), and the diameter of the impact bar used was 37.0 mm. Three different strain rates (around 200/s, 500/s, 800/s) were achieved by adjusting the loading air pressure and the stress waves in the elastic rod were collected. Each strain rate is taken as the average of three sets of valid data.

The following steps have been followed for specific data processing: collect the stress waveform in the specimen and calculate the average stress $\sigma_s(t)$, average strain rate $\dot{\varepsilon}_s(t)$, and average strain $\varepsilon_s(t)$ according to the three-wave method formulas (1), (2), and (3). Obtain the dynamic stress-strain curve of the composites and record the dynamic compressive strength, peak strain and ultimate strain. The dynamic impact toughness was obtained by integrating the stress-strain curve, whereas the impact dissipation energy (IDE) was calculated according to formula (4).

$$\sigma_s(t)=\frac{EA}{2A_s}\left[\varepsilon_i(t)+\varepsilon_r(t)+\varepsilon_t(t)\right] \tag{1}$$

$$\dot{\varepsilon}_s(t)=\frac{c}{l_s}\left[\varepsilon_i(t)-\varepsilon_r(t)-\varepsilon_t(t)\right] \tag{2}$$

$$\varepsilon_s(t)=\int_0^t \dot{\varepsilon}_s(\tau)d\tau \tag{3}$$

$$IDE=\frac{AEc}{A_s l_s}\int_0^t\left[\varepsilon_i(t)^2-\varepsilon_r(t)^2-\varepsilon_t(t)^2\right]dt \tag{4}$$

where ε_i and ε_r are the incident strain and reflection strain of the bar, respectively. ε_t is transmission strain in the bar. A is the cross-sectional area of the bar, c is the wave speed in the bar. E is the elastic modulus of the bar, A_s is the cross-sectional area of sample, l_s is the initial thickness of sample.

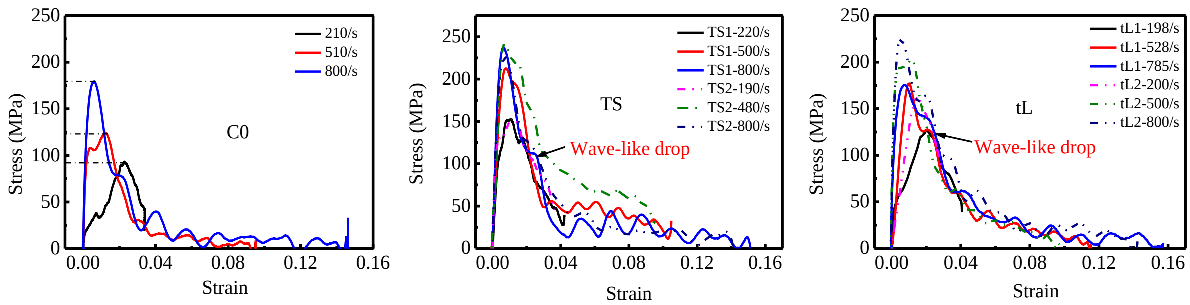
2.2.2 Morphology characterization

The field emission scanning electron microscope was used to observe the microscopic morphology of cementitious composites. Prior to the examination, the surfaces of specimens were coated with a thin gold layer using Q150T ES (Quorum Ltd.), then all these specimens were observed by SEM using Nova Nano SEM 450 machine.

3. Effect of size of untreated MWCNTs on cementitious composites

3.1 Dynamic impact stress-strain curves

Fig.2 shows the typically dynamic impact stress-strain curves of cementitious composites containing MWCNTs of different sizes and content.



(a) Composites without MNCNTs (b) Composites with thick-short MNCNTs (c) Composites with thin-long MNCNTs

Fig. 2 Dynamic impact stress-strain curves of cementitious composites containing MWCNTs of different sizes and contents

As shown in Fig. 2, there exist two stages in the dynamic impact stress-strain curves of all cementitious composites: approximately linear ascending stage and non-linear descending stage, indicating that MWCNTs do not significantly change the dynamic damage evolution of cementitious composites. However, the provision of MWCNTs prolongs the ascending curve of cementitious composites and slows down the descending section of the curve. When the strain rate is around 500/s, there even exists the wave-like drop in the curve descending section of MWCNTs reinforced cementitious composites. These phenomena show that MWCNTs increase the elastic modulus of cementitious composites and improve the toughness of the composite through enhancing the energy consumption of composites at the damage softening stage.

3.2 Dynamic compressive strength

Fig. 3 shows the dynamic compressive strength of cementitious composites reinforced with different sizes of untreated MWCNTs, whereas the relationships between dynamic compressive strength and strain rate of each composites are displayed in Fig. 4.

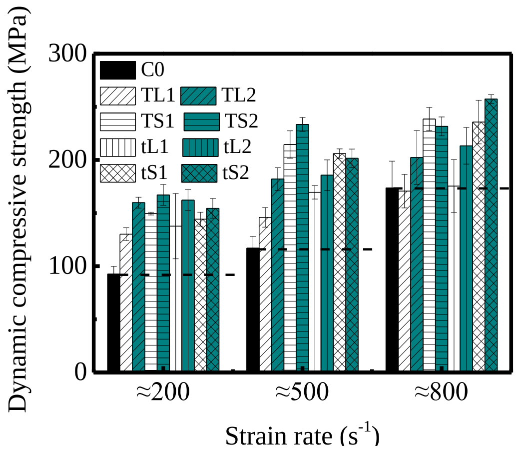
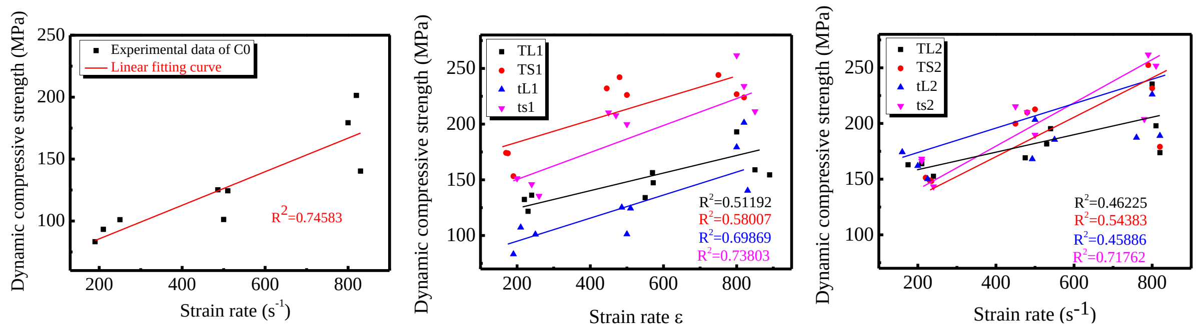


Fig. 3 Dynamic compressive strength of cementitious composites containing MWCNTs of different sizes and content

As shown in Fig. 3, the incorporation of MWCNTs significantly increases the strength of cementitious composites. When the strain rate is between 200/s and 500/s, cementitious composites with thick-short MWCNTs (TS) present the largest dynamic compressive strength, while the incorporation of thin-short MWCNTs (tS) produces the highest strength has the strain rate reaches 800/s. Within the comparable strain rates, at the strain rate of 0.25%-0.5%, the incorporation of four sizes of MWCNTs (TL, TS, tL, tS) maximumly increases the strength value of cementitious composites by 72.7%, 99.6%, 75.3% and 76.2%, respectively.

The enhancing mechanisms of MWCNTs on cementitious composites can be expressed as follows: The filling and nucleation effect of MWCNTs refine the pore volume of cement matrix and promote the cement hydration of cementitious composites [34, 35]. Meanwhile, the high thermal conductivity of MWCNTs transfers the hydration thermal stresses inside the composites, and thereby reducing autogenous shrinkage of the composite [4]. Furthermore, the disorderly distribution of MWCNTs increases the three-dimensional network structure of cementitious matrix and then enhances the structural integrity of the composites [29]. In addition, the increased polymerization degree and average molecular chain length of calcium silicate hydrate (C-S-H) gel could further improve the network structure of cementitious composites [36].



(a) Composites without MWCNTs (b) Composites with 0.25% MNCNTs (c) Composites with 0.5% MNCNTs

Fig. 4 Strain rate effect of cementitious composites containing MWCNTs of different sizes and content

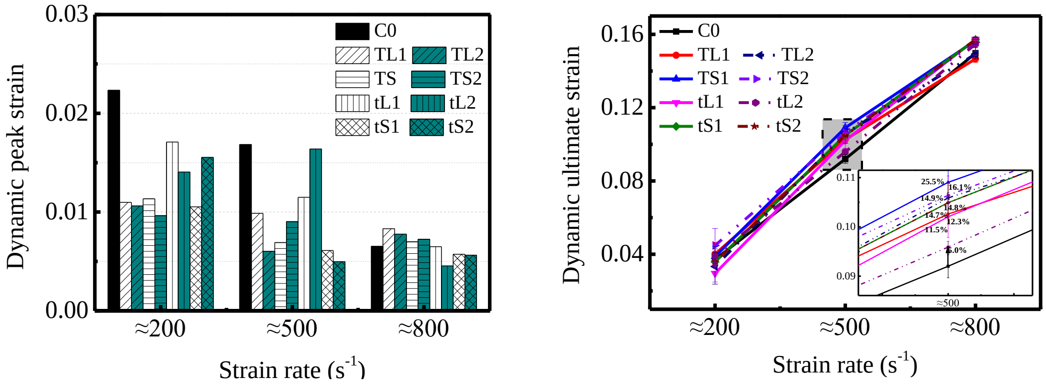
As shown in Fig. 4, all dynamic compressive strength-strain rate curves of cementitious composites satisfy linear relationship, namely, possessing the strain rate effect of the composite. Compared to control cementitious composites without MWCNTs, cementitious composites with MWCNTs show lower values of the linear fitting degree, and the reduction ranges from 1.0% to 38.5%. This phenomenon shows that the provision of MWCNTs decreases the strain rate sensitivity of cementitious composites and therefore weakens the rate-hardening phenomenon of the composite [9].

According to the damage mechanics theory, a large number of micro-cracks are formed inside the cementitious composites at high strain rates. Due to time constraints, the damage does not only occur at the weak interface of composites, but also exists in the aggregates and cement matrix, resulting in the increase of the failure stress. In addition, the increased cohesive force of free water and the occurrence of confining effect under dynamic load further increase the strength of cementitious composites [37]. However, the presence of MWCNTs increases the lateral constraint of composites through offsetting the lateral inertial force, which in turn weakens the confining pressure effect of the composites. The improved network structure of cementitious composites weakens the stress accumulation at the crack tip, which in turn effectively inhibits the generation and propagation of micro-cracks [4, 23, 34]. Furthermore, the MWCNTs of high specific surface and hollow tubular structure absorb a large amount of water [27], reducing the free water content and further weakening confining effect in the composite [38].

3.3 Dynamic compression deformation

Fig. 5a shows the dynamic peak strain of different types of MWCNTs reinforced cementitious composites, whereas the corresponding dynamic ultimate strain is shown in Fig.

5b.



(a) Dynamic peak strain (b) Dynamic ultimate strain

Fig. 5 Dynamic peak strain and dynamic ultimate of cementitious composites containing MWCNTs of different sizes and content

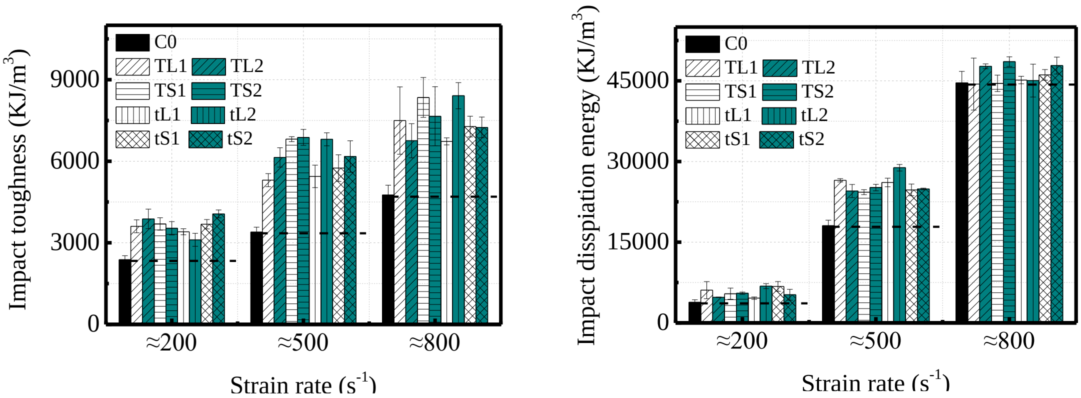
As shown in Fig. 5a, the dynamic peak strain of control cementitious composites remarkably decreases with increasing the strain rates, showing obvious dynamic embrittlement phenomenon [39]. At the medium and low strain rates, cementitious composites with MWCNTs have lower dynamic peak strain, but this this trend is reversed at high strain rate. These phenomena above indicate that the incorporation of MWCNTs (especially thick-long MWCNTs) improves the deformability of the composite at high strain rates. The dynamic ultimate strain of all composites increases with the increase of strain rate (Fig. 5b), exhibiting the strain rate effect of the composite. Compared to the linear increase of ultimate strain of control cementitious composites, the strain increase rate of MWCNTs reinforced cementitious composites first increases and then decreases. When the MWCNT content is 0.25%, composites with thick-long MWCNTs (TL) have the largest ultimate strain value, while the thin-long MWCNTs (tL) is more beneficial to increasing the strain value of the composites at the MWCNT content of 0.5%.

At medium and low strain rates, MWCNTs of high stiffness increase the elastic modulus of cement matrix and make the composite become harder [24, 40], which effectively prevent the movement of hydration products at the molecular level, decreasing the dynamic peak strain. However, at high strain rate, more micro-cracks need to be formed to consume energy, and the nano-enhancement effects of MWCNTs can fully play the advantage. On the one hand, the high compactness of MWCNTs reinforced cementitious composites increases the energy absorption and inhibits the generation of micro-cracks [21, 35]. On the other hand, MWCNTs bridging between micro-cracks and micro-pores block the potential path of cracks, force the cracks to bypass the MWCNTs to propagate and, therefore, deflect the crack propagation path [32]. What's more, the reinforced network structure of the composite redistributes the stress and promotes the occurrence of multi-directional cracking, delaying the steady propagation of micro-cracks [27, 34]. In addition, the reduction in orientation of calcium hydroxide crystal caused by MWCNTs makes the cracks along the crystal fracture path more tortuous [27].

3.4 Dynamic impact toughness

Fig. 6a shows the impact toughness of four sizes of MWCNTs reinforced cementitious composites, the impact dissipation energy of all cementitious composites is shown in Fig. 6b.

As shown in Fig. 6, the impact toughness and dissipation energy of all cementitious composites increases with increasing the strain rates, which corresponds to the strain rate effect of composites and is mainly related to the generation of more micro-cracks. Compared with control cementitious composites without MWCNT, cementitious composites containing MWCNTs of different sizes produce higher values of these two parameters. At low MWCNT content (0.25%), the composite with thick-short MWCNTs (tS) has the highest toughness value with a 100.8%increase rate, while the composite with thick-long MWCNTs (TL) maximumly increases the impact dissipation energy by 58.6%. When MWCNT content reaches 0.5%, the impact toughness of the four sizes of MWCNTs (TL, TS, tL, tS) reinforced cementitious composites increase by 57.5%, 100.8%, 60.5% and 70.9%, respectively, while the impact dissipation energy of these four composites increases by 35.7%, 43.6%, 77.7% and 76.8%, respectively.



(a) Impact toughness (b) Impact dissipation energy

Fig. 6 Impact toughness and impact dissipation energy of cementitious composites containing MWCNTs of different sizes and content

In general, short MWCNTs significantly increase the impact toughness of cementitious composites, and thin MWCNTs enhance the impact dissipation energy of the composite more evidently. This is because that short MWCNTs have better dispersion ability, which helps to enhance the network structure of cement matrix and improve the toughness of cementitious composites [27]. As for the thin MWCNTs, their high surface energy significantly enhances the overall energy of cementitious composites, contributing to increase the energy dissipation of stress waves [26]. It is of note that the energy dissipation value of all cementitious composites is significantly higher than that of the impact toughness value. However, the provision of MWCNTs leads to higher increase in the impact toughness than impact dissipated energy. This is because that under high-speed impact loading, the lateral stress of composites caused by Poisson's ratio effect leads to the confining pressure, which attenuates the strain energy in the propagation process, but it does not enhance the energy absorption ability of the composite [37]. The presence of MWCNTs weakens the confining pressure effect of cementitious composites, which in turn reduces the stress wave dissipation to some extent.

4. Effect of special structure and coating treatment of MWCNTs on cementitious composites

4.1 Dynamic impact stress-strain curves

Fig. 7 shows the typically dynamic impact stress-strain curve of different special types of MWCNTs reinforced composites at different strain rates.

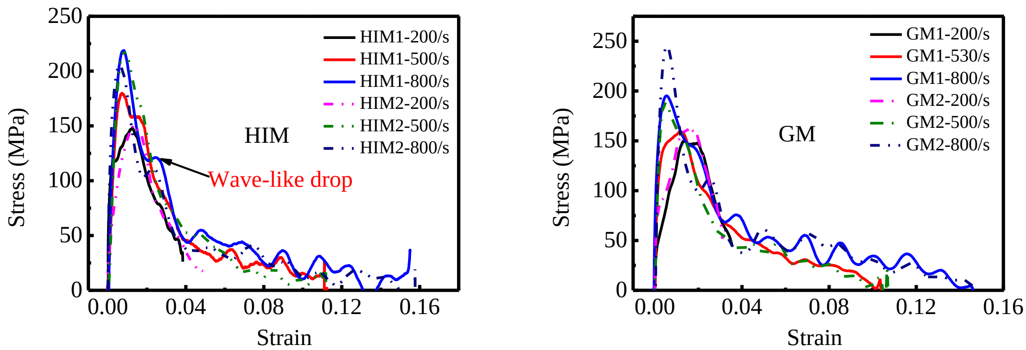


Fig. 7 Dynamic impact stress-strain curve of different special types and content of MWCNTs reinforced cementitious composites

As shown in Fig. 7, the dynamic impact stress-strain curve of special types of MWCNTs reinforced cementitious composites is similar to that of the composite with untreated MWCNTs. The whole stress-strain curve is divided into approximate linear ascending section and nonlinear descending section. With the increase of strain rate, the ascending section of the curve gradually lengthens and the descending section gradually slows down. This again shows that in the form of dynamic damage evolution, there is no difference between the composites with special types of MWCNTs and control cementitious composites. However, the wave-like drop appeared in the curve descending section of MWCNTs reinforced cementitious composites indicates that MWCNTs inhibit cracks propagation and effectively improve the damage softening of the composites.

4.2 Dynamic compressive strength

Fig. 8 shows the dynamic compressive strength of cementitious composites containing special types of MWCNTs. The relationship between dynamic compressive strength and strain rate of composites is shown in Fig. 9.

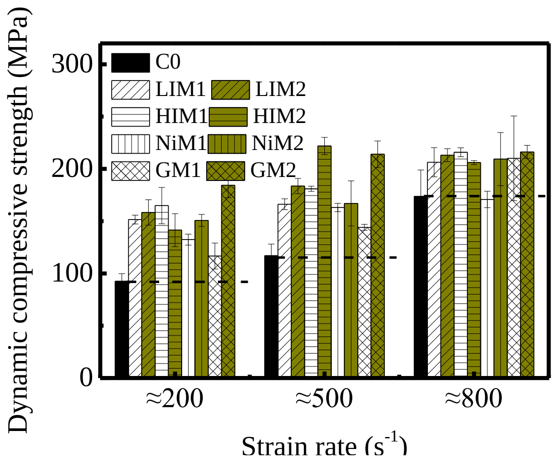
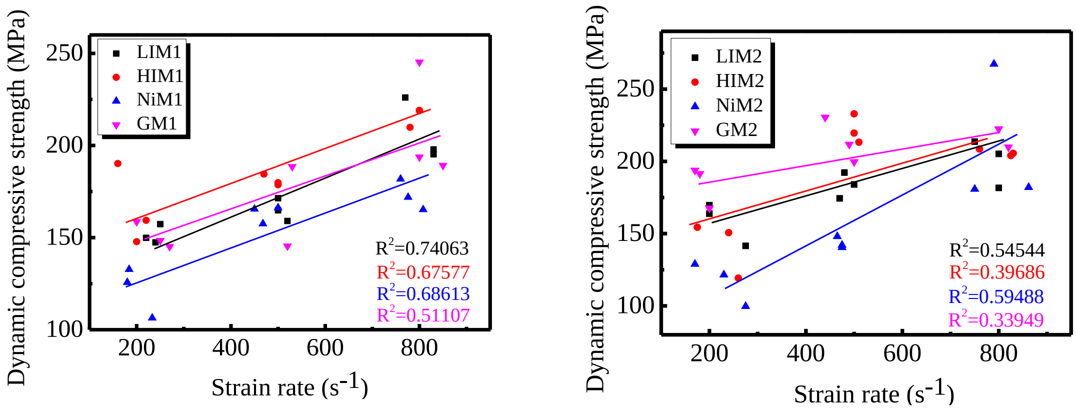


Fig. 8 Dynamic compressive strength of different special types and contents of MWCNTs reinforced cementitious composites compared to control cementitious composites

As shown in Fig. 8, similar to the strength development of untreated MWCNTs, the incorporation of all special types of MWCNTs increases the dynamic compressive strength of cementitious composites. When the MWCNT content is 0.25%, cementitious composites with helical MWCNTs (HIM) have the largest dynamic compressive strength, while the composite with graphitized MWCNTs (GM) present higher strength value at the MWCNT content of 0.5%. Within the comparable strain rates, the incorporation of four special types of MWCNTs (LIM, HIM, NiM, GM) maximumly increases the dynamic compressive strength of cementitious composites by 71.1%, 89.8%, 43.0% and 99.1%, respectively.

In general, most special types of MWCNTs have stronger effect on the strength increase of cementitious composites than untreated MWCNTs. This is consistent with the study of Cui et al. [27] under static compression loading. As for the lower strength increase of composites with nickel-coated MWCNTs, it may be related to the poor dispersion of nanotubes, causing some agglomeration of MWCNTs in the cementitious composites. Comparing to coated MWCNTs, the graphitized MWCNTs (GM) have higher strength enhancement effect than nickel-coated MWCNTs (NiM), whereas for special structure MWCNTs, the helical MWCNTs (HIM) show a larger strength increase than the large inner diameter thin-walled MWCNTs (LIM). This is because that helical MWCNTs can effectively reduce the sliding between graphene layers of nanotubes, meanwhile, the increased contact area between MWCNTs and hydration products contributes to playing the nano-enhancement effects of nanotubes [41]. In addition, the graphitized MWCNTs remove the amorphous carbon on their surface, and reduce the structural defects of the transistors [42]. Their unique spiral cone structure can also play a role in fiber anchoring, helping to increase the strength of cementitious composites [42].



(a) Composites with 0.25% MNCNTs (b) Composites with 0.5% MNCNTs

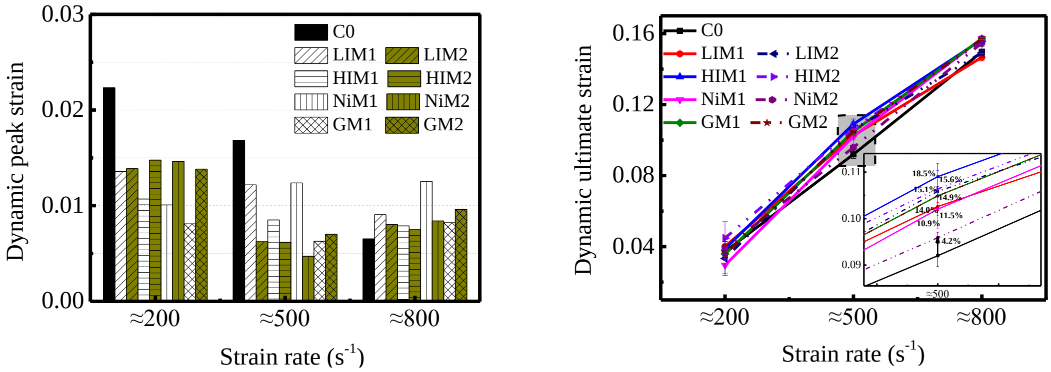
Fig. 9 Strain rate effect of different special types and content of MWCNTs reinforced cementitious composites compared to control cementitious composites

As shown in Fig. 9, cementitious composites reinforced with special types of MWCNTs have lower linear fit degree of dynamic stress-strain curves with respect to the control cementitious composites, more evident for composites modified with higher content of MWCNTs. When the MWCNT content is 0.5%, cementitious composites with graphitized MWCNTs and helical MWCNTs result in 55.5% and 46.8% reduction in fitting degree, respectively. All these phenomena above indicate that the incorporation of special types of MWCNTs reduces the strain rate sensitivity of the composite, and also the MWCNT content plays a significant role in the sensitivity change.

As early mentioned in this paper, the rate-hardening phenomenon of cementitious composites is related to the development of micro-cracks, the cohesive effect of pore water and the inertia restraint of composites [9, 37]. The presence of MWCNTs can well weaken the phenomenon by three ways: reducing the content of free water, weakening the lateral constraint of the composite material and redistributing the stress to increase the energy consumption. The influence mechanisms of special types of MWCNTs on cementitious composites are similar to that of untreated MWCNTs, explained above for untreated MWCNTs in Section 3.1.

4.3 Dynamic compression deformation

Fig. 10a shows the dynamic peak strain of special types of MWCNTs reinforced cementitious composites compared to control cementitious composites, the corresponding dynamic ultimate strain of these cementitious composites is shown in Fig. 10b.



(a) Dynamic peak strain (b)Dynamic ultimate strain

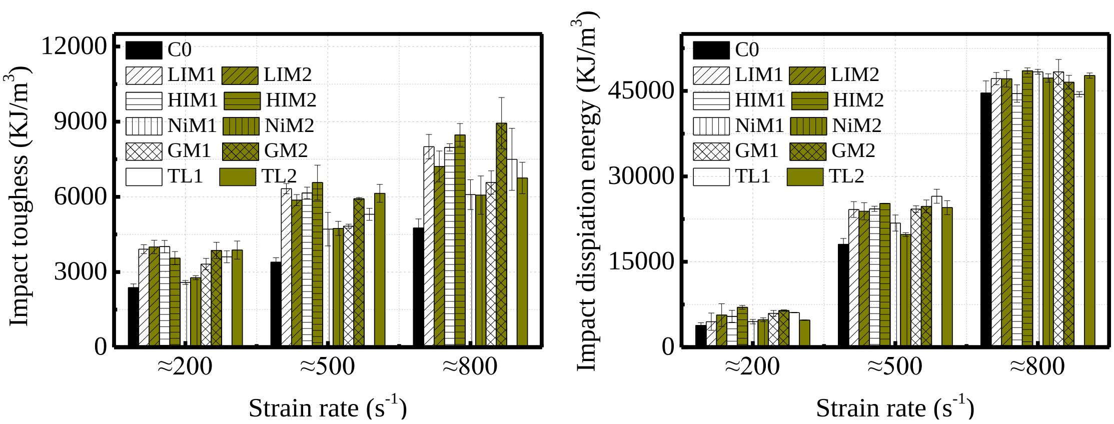
Fig. 10 Dynamic peak strain and dynamic ultimate strain of different special types and content of MWCNTs reinforced cementitious composites

As shown in Fig. 10, all the MWCNTs reinforced cementitious composites have lower dynamic strain with respect to control cementitious composites at low and medium strain rates, but present higher strain value at high strain rate. This indicates that the incorporation of special types of MWCNTs mainly improves the deformation capacity of cementitious composites at the high strain rate, leading to higher ductility of the composite. Within the comparable strain rates, the incorporation of nickel-coated MWCNTs significantly increases the dynamic peak strain of cementitious composites, while the incorporated helical MWCNTs evidently enhance the dynamic ultimate strain of the composite. Through comparison, it can be found that the coating treated MWCNTs contribute to inhibit the formation and steady propagation of cracks, and the MWCNTs with special structure are more conducive to delay the unsteady propagation of cracks. This may be because, in the former stage, the filling effect and nuclear effect of MWCNTs play a leading role [43, 44], while the network enhancement effect of MWCNTs plays a more important role in the latter stage [38].

Compared to MWCNTs with special structures, the increased surface activation point of coating treated MWCNTs enhances the interface bond strength between nanotubes and cement matrix, thereby increasing the cohesive force of cementitious composites [45]. Additionally, the nickel-coated MWCNTs of high thermal conductivity contribute to transfer the hydration thermal stress of cement matrix, further reducing the initial defects of the composites and inhibiting the generation of micro-cracks [21, 44]. For the helical MWCNTs, their unique spring structure have good resilience or time-delay, which can convert the kinetic energy of the composite into time-delay strain energy and then dissipate it in the form of heat energy [46]. The absorbing energy ability of cementitious composites is increased and the crack propagation is delayed [47]. Furthermore, the helical MWCNTs enhance the network structure of cementitious composites, which makes the stress distribution more uniform and induces the multi-directional cracking [48]. The equivalent reinforcement effect of helical MWCNTs further increases the adhesion force between nanotubes and composites, thereby enhancing the bonding energy required for the MWCNTs pulling out. As for the toughening advantage of graphitized MWCNTs, it may be related to the improved micro-structure: The graphite morphology of internal chaotic layers is transformed into lamellar structure and the external amorphous carbon is graphitized (from amorphous to crystalline) [30], which in turn enhances the van der Waals force between molecules and improves the micro-structure of MWCNTs.

4.4 Dynamic impact toughness

Fig. 11a shows the impact toughness of special types of MWCNTs reinforced cementitious composites compared to control cementitious composites, the corresponding impact dissipation energy of these cementitious composites is shown in Fig. 11b.



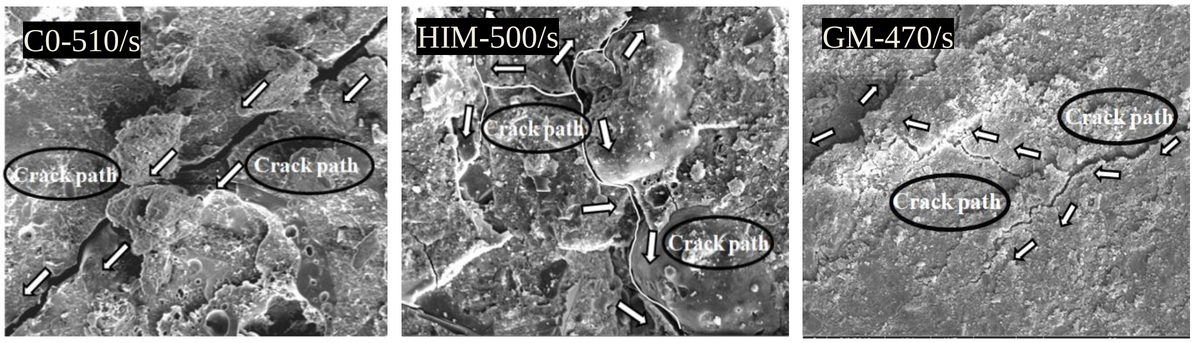
(a) Composites with 0.25% MNCNTs (b) Composites with 0.5% MNCNTs

Fig. 11 Impact toughness and impact dissipation energy of different special types and content of MWCNTs reinforced cementitious composites compared to control cementitious composites

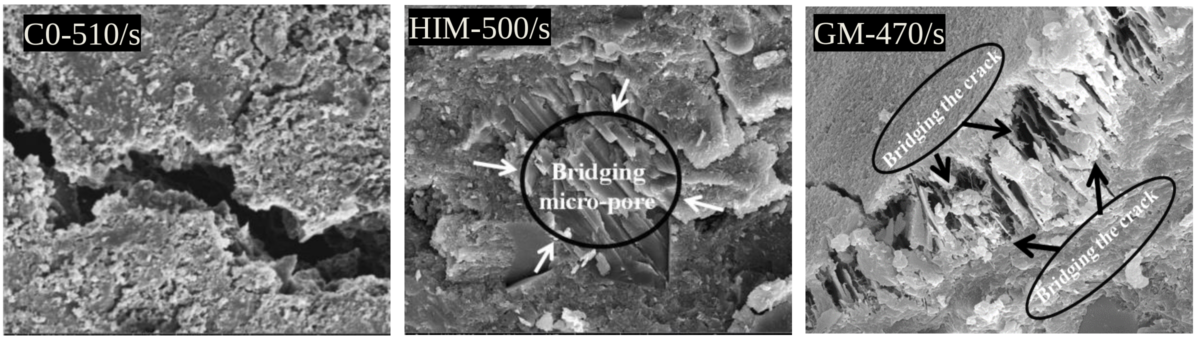
As shown in Fig. 11, cementitious composites with special types of MWCNTs have higher impact toughness values and impact dissipation energy compared with the control composite. When the MWCNT content is 0.25%, the composite with helical MWCNTs (HIM) has the largest toughness values with 81.5% increase rate than that of the control composite. When the MWCNT content is 0.5%, the impact toughness of cementitious composites can be increased by 93.8% and 87.9%, respectively with the incorporation of helical MWCNTs (HIM) and graphitized MWCNTs (GM). As for the impact dissipation, cementitious composites with 0.25% HIM can increase the dissipation energy by 82.6%, while the increase values are up to 67.8% when the at the GM content of0.5%. Compared to the composites with untreated MWCNTs, these two special types of MWCNTs reinforced cementitious composites even present 25.4% and 32.3% higher impact toughness and 18.6% and 35.2% increase of impact dissipation energy, respectively. This is mainly related to the unique spring structure of helical MWCNTs and the high crystallinity of graphitized MWCNTs, which increase the energy absorption capacity of cementitious composites and better exert the nano-enhancement effects of the nanotubes.

4.5 Reinforcing mechanisms of MWCNTs

In order to authentically show the reinforcing mechanisms of MWCNTs on cementitious composites, this paper observes the micro morphology of special types of MWCNTs reinforced cementitious composites compared to the control composite. The SEM images of cementitious composites at different strain rates are shown in Figs. 12 and 13.



(a) Propagation path of cracks



(b) Bridging of MWCNTs

Fig. 12 SEM of MWCNTs reinforced cementitious composites compared with control cementitious composites

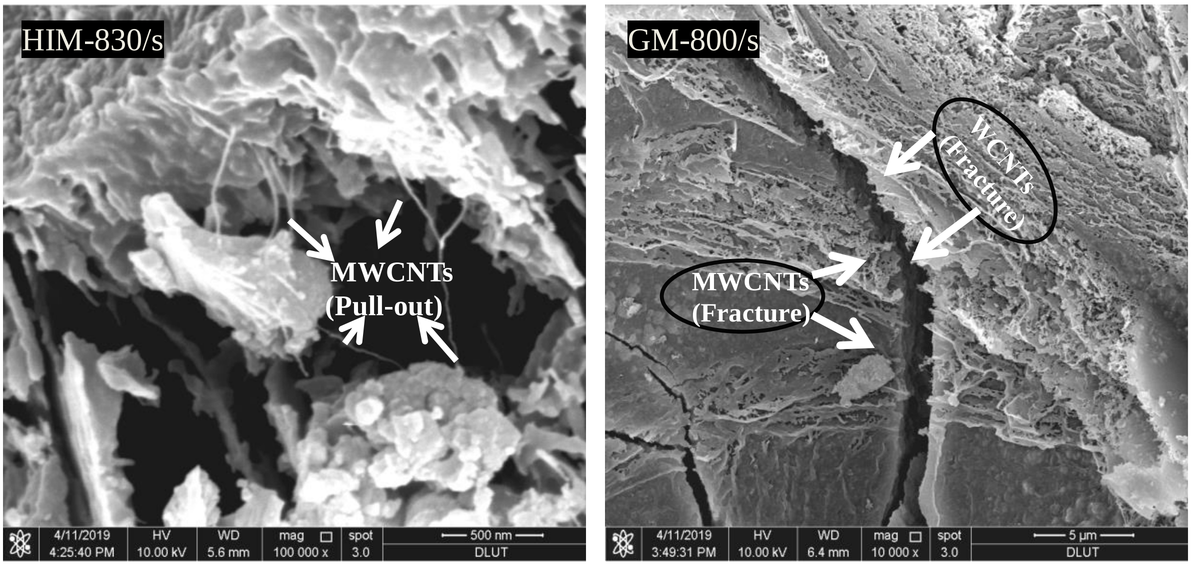


Fig. 13 Pulling out and fracture of MWCNTs

As shown in Fig. 12a, compared with control cementitious composites, cementitious composites with special types of MWCNTs at medium strain rate make the crack path inside the body obviously deflected, even causing the phenomenon of multi-directional cracking. This indicates that the incorporation of MWCNTs improves the network structure of the composite, making the stress distribution in the matrix becomes uniform. In the crack formation zone, the MWCNTs of strong bond strength work as fiber-bridging role, block the crack propagation path, and delay the crack development (as seen from Fig. 12b). When the strain rate reaches 800/s (Fig. 13), the brittle failure occurs inside the control cementitious composites due to the high incident energy. However, some damage occurs inside the MWCNTs reinforced composites, the phenomenon of MWCNTs pulling-out and fracture exist in and around the damage zone. In this manner, the toughness of cementitious composites is increased and the brittle failure of the composite materials is weakened. In fact, the reinforced network structure of MWCNTs can offset the inertial stress inside the cementitious composites, and therefore, enhance the confining pressure of the composite. Furthermore, the pull-out and fracture of MWCNTs overcome the friction force between MWCNTs and cement matrix, further absorbing the strain energy released by the crack and delaying the crack propagation [30].

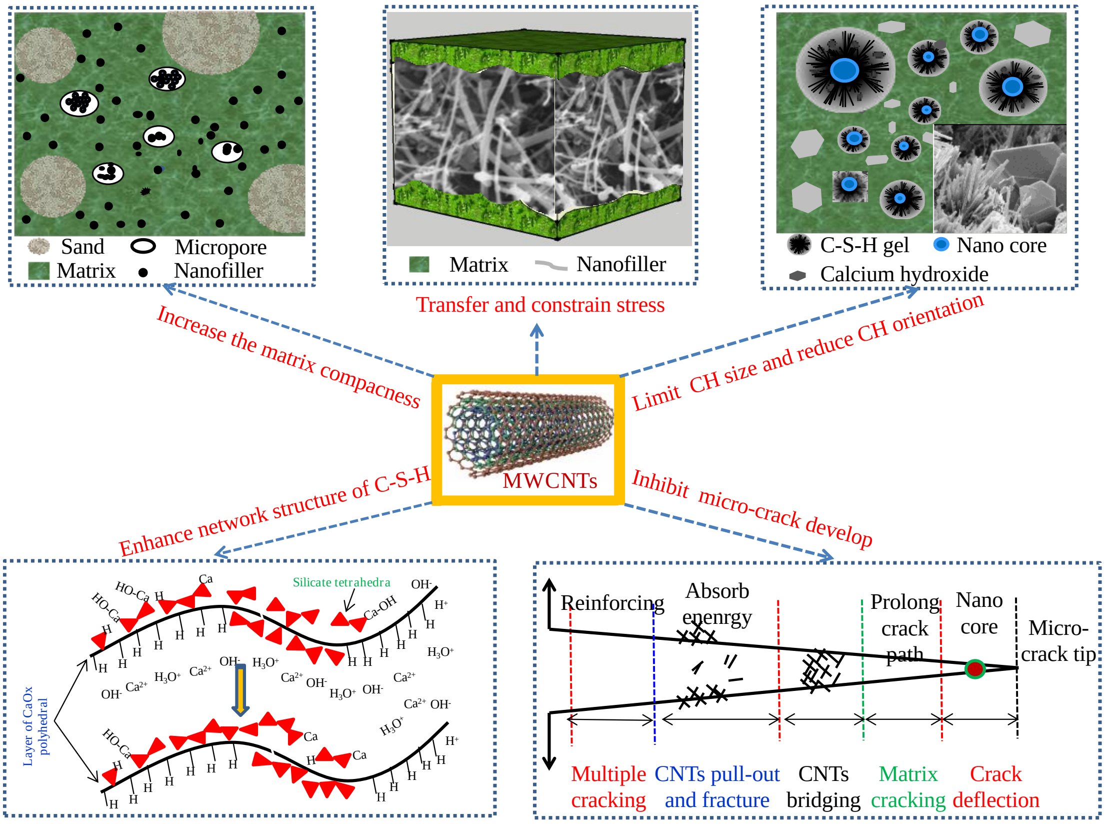


Fig. 14 Schematic diagram of reinforcing mechanism of MWCNTs on cementitious composites

In order to intuitively reflect the modification effect of nanotubes, the reinforcing mechanism diagram of MWCNTs on cementitious composites is displayed in Fig.14. Based on the results from literatures [12, 21, 25-27, 32, 48], MWCNTs improve the structural integrity of cementitious composites by improving the microstructure of cement matrix and regulating the morphology of hydration products. Meanwhile, the network structure and bridging effect of MWCNTs further inhibit the development of cracks and, therefore, improve the toughness of materials. Compared to short MWCNTs, long MWCNTs of high aspect ratio can increase the contact area with the hydration products, attract more hydration products to deposit on its surface, and thereby better exert the nucleation effect of MWCNTs. Furthermore, the crack is difficult to bypass the long MWCNTs but directly pass through it, which significantly plays the micro-fiber effect of the MWCNTs.

5 Conclusions

In this paper, eight types of MWCNTs were selected to modify the cementitious composites, and the split Hopkinson pressure bar was used for impact compression test. The dynamic mechanical properties of MWCNTs reinforced cementitious composites with different sizes, special structures and coating treatments were studied, and the toughening mechanisms of MWCNTs on the composite were discussed. Finally, the dynamic damage evolution behavior of cementitious composites was confirmed and the dynamic compression toughness were characterized. Conclusions are summarized as follows:

1) All types of MWCNTs can increase the dynamic compressive strength and ultimate strain of cementitious composites at different strain rates, but only enhance the peak strain of MWCNTs reinforced cementitious composites at high strain rates.

2) For untreated MWCNTs, the short MWCNTs contribute to increase the dynamic compressive strength of cementitious composites because of their good dispersion, while the long MWCNTs are more conducive to improve the deformability of the composite due to the nucleation and bridging effect of nanotubes. Among all mixes, cementitious composites with thick-short MWCNTs exhibit the highest impact toughness with a 100.8% increase compared to control cementitious composites, while the composite with thin-long MWCNTs maximumly increase the impact dissipation energy by 77.7%.

3) MWCNTs with special structures and coating treatments have higher strength increase advantages for cementitious composites than untreated MWCNTs. At MWCNT content of 0.5%, cementitious composites with helical MWCNTs maximumly increase the impact toughness and dissipation energy by 93.8% and 82.6%, respectively as compared to control cementitious composites. Compared with cementitious composites with untreated MWCNTs, the impact toughness and dissipation energy of the composite with special types of MWCNTs are increased by 32.3% and 35.2%, respectively.

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References

[1] J. S. Zhu, J. Y. Xu, E. Bai, X. Luo, Y. Gao. Effect of composite nanomaterials on dynamic mechanical properties of concrete. Acta Materiae Compositae Sinica. 2016, 33(3): 597-605.

[2] S. Agrawal, K. K. Singh, P. K. Sarkar. Impact damage on fiber-reinforced polymer matrix composite–a review. Journal of Composite Materials. 2014, 48(3): 317-332.

[3] B. G. Han, X. Yu, J. P. In: Self-Sensing Concrete in Smart Structures, Publisher: Elsevier, 2014, 385p.

[4] B. G. Han, L. Q. Zhang, J. P. Ou. In: Smart and multifunctional concrete toward sustainable infrastructures, Publisher: Springer, 2017, 400p.

[5] E. García-Macías, A. D'Alessandro, R. Castro-Triguero, D. Pérez-Mira, F. Ubertini. Micromechanics modeling of the uniaxial strain-sensing property of carbon nanotube cement matrix composites for SHM applications. Composite Structure. 2017, 163: 195-215.

[6] S. F. Dong,B. G. Han, X. Yu,J.P. Ou. Dynamic impact behaviors and constitutive model of super-fine stainless wire reinforced reactive powder concrete. Construction and Building Materials. 2018, 184: 602-616.

[7] Q. Fang, J. Hong, J. H. Zhang, L. Chen, Z. Ruan. Issues of SHPB test on concrete-like material. Engineering Mechanics. 2014,31(5): 1-14 (In Chinese).

[8] S. Sasmal, N. Ravivarman, B. S. Sindu, Vignesh. Electrical conductivity and piezo-resistive characteristics of CNT and CNF incorporated cementitious nanocomposites under static and dynamic loading. Composites Part A: Applied Science and Manufacturing. 2017, 100: 227-243.

[9] M. J. Forrestal, T. W. Wright, W. Chen. The effect of radialinertia on brittle samples during the split Hopkinsonpressure bar test. International Journal of Engineering Science. 2007, 34(3): 405-411.

[10] S. Xu, Q. Li. Theoretical analysis on bending behavior of functionally graded composite beam crack-controlled by ultra-high toughness cementitious composites. Science in China Series E: Technological Sciences. 2009, 52(2): 363-378.

[11] V. C. Li, C. K. Y. Leung. Theory of steady state and multiple cracking of random discontinuous fiber reinforced brittle matrix composites. Journal of Engineering Mechanics. 1992, 118(11): 2246-2264.

[12] A. M. Okeil, S. EI-Tawil, M. Shahawy. Short-term tensile strength of carbon fiber-reinforced polymer laminates for flexural strengthening of concrete girders. ACI Structural Journal. 2001, 98(4): 470-478.

[13] T. Y. Lim, P. Paramasivam, S. L. Lee. Analytical model for tensile behavior of steel-fiber concrete. ACI Materials Journal. 1987, 84(4): 286-298.

[14] C. Zweben. Tensile failure of fiber composites. AIAA Journal. 1968, 6(12): 2325-2331.

[15] R. Sharma, Z. Iqbal. In situ observations of carbon nanotube formation using environmental transmission electron microscopy. Applied Physics Letters. 2004, 84(6): 990-992.

[16] A. Montazeri, J. Javadpour, A. Khavandi, A. Tcharkhtchi, A. Mohajeri. Mechanicalproperties of multi-walled carbon nanotube/epoxy composites. Materials and Design. 2001, 31:4202-4208.

[17] J. D. Fidelus, E. Wiesel, F. H. Gojny, K. Schulte, H. D. Wagner. Thermo-mechanical properties of randomly oriented carbon/epoxy nanocomposites. Composites Part A: Applied Science and Manufacturing. 2005, 36(11): 1555-1561.

[18] Z .Ounaies, C. Park, K. E. Wise, E. J. Siochi, J. S. Harrison. Electrical properties of single-wall carbon nanotube reinforced polyimide composites. Composites Science and Technology. 2003, 63(11): 1637-1646.

[19] M. Micheli, C. Apollo, R. Pastore, R. B. Morles, S. Laurenzi, M. Marchetti. Nanostructured composite materials for electromagnetic interference shielding applications. Acta Astronautic. 2011, 69(9-10): 747-757.

[20] H. Huang, C. Liu, Y. Wu, S. Fan. Aligned carbon nanotube composite films for the thermal management. Advanced Materials. 2005, 17(13): 1652-1656.

[21] G. Y. Li, P. M. Wang, X. Zhao. Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. Carbon. 2005, 43(6): 1239-1245.

[22] A. Cwirzen, K. Habermehl-Cwirzen, V. Penttala. Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. Advances in Cement Research. 2008, 20(2): 65-73.

[23] B. G. Han, S. W. Sun, S. Q. Ding, L. Q. Zhang, X. Yu, J. P. Ou. Review of nanocarbon-engineered multifunctional cementitious composites. Composites Part A: Applied Science and Manufacturing. 2015, 70: 69-81

[24] Y. Saez de Ibarra, J. J. Gaitero, E. Erkizia, I. Campillo. Atomic force microscopy and nanoindentation of cement pastes with nanotube dispersions. Physica Status solidi (a). 2006, 203(6): 1076-1081.

[25] F. Collins, J. Lambert, W. H. Duan. The influences of admixtures on the dispersion, workability, and strength of carbon nanotube–OPC paste mixtures. Cement and Concrete Composites. 2012, 34(2): 201-207.

[26] R. K. A. Al-Rub, A. I. Ashour, B. M. Tyson. On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. Construction and Building Materials. 2012, 35(10): 647-655.

[27] X. Cui, B. G. Han, Q. F. Zheng, X. Yu, S. F. Dong, L. Q. Zhang, J. P. Ou. Mechanical properties and reinforcing mechanisms of cementitious composites with different types of multiwalled carbon nanotubes. Composites Part A: Applied Science and Manufacturing. 2017, 103: 131-147.

[28] Y. F. Ruan, B.G. Han, X. Yu, W. Zhang, D. N. Wang. Carbon nanotubes reinforced reactive powder concrete. Composites Part A: Applied Science and Manufacturing. 2018, 112: 371-382.

[29] J. M. Makar, G. W. Chan. Growth of cement hydration products on single walled carbon nanotubes. Journal of the American Ceramic Society. 2010, 92(6): 1303-1310.

[30] J. M. Makar, J. Margeson, J. Luh. Carbon nanotube/cement composites-early results and potential applications. In: Proceedings of the 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications, Vancouver, Canada, 2005. 10p.

[31] B. M. Tyson, R. K. Abu Al-Rub, A. Yazdanbakhsh, Z. Grasley. Carbon nanotubes and carbon nanofibers for enhancing the mechanical properties of nanocomposite

cementitious materials. Journal of Materials in Civil Engineering. 2011, 23(7): 1028-1035.

[32] S. Rana, R. A. Fangueiro. A review on nanomaterial dispersion, microstructure, andmechanical properties of carbon nanotube and nanofiber reinforcedcementitious composites. Journal of Nanomaterials. 2013, 80(7): 1-19.

[33] P. C. Ma, N. A. Siddiqui, G. Marom, J. K. Kim. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. Composites Part A: Applied Science and Manufacturing. 2010, 41(10): 1345-1367.

[34] L. Q. Zhang, S. Q. Ding, L. W. Li, S. F. Dong, D. N. Wang, X. Yu, B. G Han. Effect of characteristics of assembly unit of CNT/NCB composite fillers on properties of smart cement-based materials. Composites Part A: Applied Science and Manufacturing. 2018, 109: 303-320.

[35] T. Nochaiya, A. Chaipanich. Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials. Applied Surface Science. 2011, 257(6): 1941-1945.

[36] J. L. Wang, B. G. Han, Z. Li, X. Yu, X. F. Dong. Effect Investigation of nanofillers on C-S-H gel structure with Si NMR. Journal of Materials in Civil Engineering. 2018, 31(1): 04018352.

[37] J. Xu, D. Zhao, F. Fan, Dynamic characteristics of fiber reinforced concrete. Northwestern Polytechnical University Press, 2013 (In Chinese).

[38] J. L. Wang, S. F. Dong, D. N. Wang, X. Yu, B. G. Han, J. P. Ou. Enhanced impact properties of concrete modified with nanofiller inclusions. Journal of Materials in Civil Engineering. 2019, 31(5): 04019030.

[39] X. T. Wu, S. S. Hu, D. X. Chen, Z. Q. Yu. Experimental study on impact compression of steel fiber high strength concrete. Explosion and Shock Waves. 2005, 25(2): 125-131 (In Chinese).

[40] S. Wansom, N. J. Kidner, L. Y. Woo, T. O. Mason. AC-impedance response of multi-walled carbon nanotube/cement composites. Cement and Concrete Composites. 2006, 28(6): 509-519.

[41] J. Q. Huang, Q. Zhang, F. Wei. Coiled carbon nanotubes. Progress in Chemistry. 2009,

21(4): 637-643.

[42] Z. M. Lu, D. L. Zhao, Y. F. Liu, Z. M. Shen. Effect of graphitization on the structure of carbon nanotubes. Transactions of Materials and Heat Treatment. 2005, 26(6): 9-11.

[43] J. P. Fu, J. L. Yang, L. K. Yin, W. Liu, J. Wang, Z. Chen. Dynamic properties of zirconia ceramic bullets under high-speed impact. Journal of the Chinese Ceramic Society.2016, 44(2): 346-352 (in Chinese).

[44] B. G. Ma, H. N. Li, J. P. Mei, L. Han, F. G. Chen. Toughening effect and mechanism of nano-titanium dioxide on cement-based materials. Journal of Functional Materials. 2000, 46(12): 12065-12069 (in Chinese).

[45] S. Arai, M. Endo. Carbon nanofiber-copper composites powder prepared by electrodeposition. Electrochemistry Communications. 2003, 5(9): 797-799.

[46] K. M. Liew, M. F. Kai, L. W. Zhang. Mechanical and damping properties of CNT-reinforced cementitious composites. Composite Structure. 2017, 160: 81-88.

[47] K. T. Lau, M. Lu, D. Hui. Coiled carbon nanotubes: Synthesis and their potential applications in advanced composite structures. Composites Part B: Engineering. 2006, 37(6): 437-448.

[48] D. Qian, E. C. Dickey, R. Andrews, T. Rantell. Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. Applied Physics Letters. 2000, 76(20): 2868-2870.